

Estimation of the Krichevskii Parameter for Aqueous Nonelectrolytes

A.V. Plyasunov and E.L. Shock
Department of Earth and Planetary Sciences
Washington University
St. Louis, MO 63130 U.S.A.

The biggest challenge facing any predictive model for calculating the infinite dilution thermodynamic properties of aqueous nonelectrolytes is to provide a correct description of the sign and magnitude of the divergence of the partial molar properties of a solute in the vicinity of the critical point of pure water. As the thermodynamics of infinitely dilute solutions near the solvent's critical point are governed by the value of the Krichevskii parameter, A_{Kr} , it would be useful to generate estimates of this property. Various methods for evaluating A_{Kr} from experimental data are used to obtain the values of the Krichevskii parameter for about thirty aqueous nonelectrolytes, with wide variations in polarity (from helium to boric acid and dissolved silica) and sizes (from ammonia to n-dodecane). These "experimental" values of A_{Kr} are used to test the possibility of predicting the Krichevskii parameter from the van der Waals and Peng-Robinson equations of state in combination with the "one-fluid" van der Waals mixing rules. Such a test shows that these predictions are useful only for nonpolar solutes of small sizes. We propose an empirical correlation between A_{Kr} and the Gibbs energy of hydration (at 298.15 K and 0.1 MPa) for the corresponding compound, which is apparently a better alternative (at least for polar compounds and solutes of large sizes). This correlation seems to hold for solutes with values of the Krichevskii parameter ranging from -200 to +200 MPa, and values of the Gibbs energy of hydration extending over 100 kJ·mol⁻¹, and allows predictions of the sign and the magnitude of A_{Kr} for many aqueous organic and inorganic solutes. For example, this correlation predicts negative values of the Krichevskii parameter for aqueous amino acids, in agreement with the recent experimental results of Clarke and Tremaine (1999).